

Thermodynamic Properties of Fluorinated Ethers and Ketones as Alternative Refrigerants

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Abstract

We measured critical properties and normal boiling points of five fluorinated ethers and two fluorinated ketones using modified static-type apparatuses. The advantage of the measuring apparatuses was that a small amount of a sample was enough to determine the thermodynamic properties accurately. The uncertainties for the measurement were $\pm 30\text{mK}$ in temperature, $\pm 2\text{kPa}$ in pressure and $\pm 0.2\%$ in density for the critical properties, and $\pm 10\text{mK}$ for the normal boiling point, respectively. Lydersen's group contribution

method estimated the critical properties fairly well, but no group contribution method could predict the normal boiling point reasonably.

Introduction

We are investigating many kinds of thermodynamic properties including critical properties, normal boiling point, vapor pressure, PVT relation and viscosity for a series of fluorinated compounds such as ethers, alcohols, ketones and others. They are expected to be new generation alternatives for CFC and HCFC used currently and to have lower ozone-depletion indices and smaller global warming effects, together with high performance as refrigerants, blowing agents or cleaning fluids.

In this work, we measured the critical properties and the normal boiling points of five fluorinated ethers and two fluorinated ketones and examined the applicability of group contribution techniques to the prediction of the critical properties and the normal boiling points.

Experimental Section

A schematic diagram of an apparatus used for the measurement of critical properties is shown in Fig.1. It consists of a view cell (A), an expansion vessel to discharge a sample (B) and measuring devices of temperature and pressure. The first two vessels are placed in a thermostated oil bath (G) controlled by electric heaters (F1, F2). The view cell with 5.3 cm³ inner volume is designed for a maximum working pressure of 7 MPa

and maximum working temperature of 473 K and, on both sides of the cell, 10 mm thick sapphire windows are placed to observe the behavior of the meniscus between the vapor and liquid phases.

The critical temperature of the sample was measured using a platinum resistance thermometer (T) inserted into the aluminum block mounted around the view cell. The critical pressure was measured by a differential pressure null gauge (C), a differential pressure null indicator (D) and a precise pressure gauge (P1). In order to avoid the error caused by the condensation of the vapor of the sample, we determined the vapor pressure of the sample by measuring the pressure of nitrogen gas supplied to the one side of a thin metallic diaphragm placed in the chamber of the differential pressure null gauge, where the pressure of the nitrogen gas was well-balanced with the vapor pressure of the sample in the opposite side of the diaphragm. The critical density was determined from the mass of the sample confined in the view cell at the critical point, where the inner volume of the cell was calibrated by filling water with a known density.

The experimental procedure is described below. The sample was degassed in a reservoir by successive evaporate-condensate cycles under vacuum to remove non-condensable gases, and then it was transferred to the evacuated view cell in the oil bath. The temperature of the oil bath was increased gradually as observing the existence of the meniscus. The meniscus disappeared and the strong critical opalescence was observed in a close vicinity of the critical point. The temperature and pressure at the maximum critical opalescence was recorded. Then the temperature was raised a little above the critical temperature to reach a uniform phase of a supercritical fluid and decreased slowly. The temperature and pressure at the reappearance of the meniscus and maximum

critical opalescence was recorded again. The critical temperature and pressure were assumed to be the mean values obtained from these two measurements. In order to determine accurate critical properties, it was important to keep the meniscus level at the middle of the view cell during the measurements.

The experimental uncertainties were estimated to be within ± 30 mK in the critical temperature, ± 2 kPa in the critical pressure and $\pm 0.2\%$ in the critical density, respectively.

A schematic diagram of an apparatus for the measurement of normal boiling points is shown in Fig.2. It consists of an equilibrium cell placed in a water bath, temperature and pressure measurement devices. The equilibrium cell (A) with 2cm^3 in internal volume was designed for a maximum working pressure of 500 kPa and maximum working temperature of 353 K. The cell was placed in the water bath (G) controlled by electric heater (D) and coolers (E, F) within an accuracy of 0.01 K. The equilibrium temperature of the sample was measured with a calibrated platinum resistance thermometer (T1), and the vapor pressure was measured by a differential pressure cell (H) and a precise pressure gauge (P1). The experimental uncertainty was estimated to be within ± 10 mK in temperature and ± 0.2 kPa in pressure.

The samples were distilled and purified by preparative-scale gas chromatograph. The collected fraction was dried over molecular sieves to remove water completely. The chemical formula and purity of the samples are presented in Table 1.

Results and Discussion

We had an experimental error to determine the accurate critical properties by the visual observation. Figure 3 shows the extent of the uncertainties for the determination of the critical temperature and pressure of a fluorinated ether using the experimental apparatus shown in Fig.1. The first uncertainty was the disagreement between the critical properties determined from the disappearance of the meniscus on increasing the temperature (Case 1) and those determined from the reappearance on decreasing the temperature (Case 2). This gave an uncertainty of 20-30 mK in the critical temperature and of 1-3 kPa in the critical pressure. The second one was the indistinctness of the maximum critical opalescence at the critical point. There was a temperature region of 20-40 mK and a pressure region of 1-2 kPa where the intensity of the opalescence was almost same. The final values were the averages of the each step as shown in Fig.3. Judging from the experiments, the experimental uncertainties were estimated to be within ± 30 mK in the critical temperature, ± 2 kPa in the critical pressure and $\pm 0.2\%$ in the critical density, respectively.

To check the reliability of the experimental apparatus and procedure, we measured the critical properties of HCFC-142b (CH_3CClF_2). Our data agreed well with the literature values (1).

The experimental results of the critical properties of fluorinated ethers and ketones are given in Table 1. No experimental data on the critical properties were available in literatures. The experimental data were compared with the Lydersen's estimation (2), which is one of successful group contribution methods. The calculated results are also given in Table 1. This method could estimate the critical properties of the fluorinated compounds fairly well, although it was developed mainly to apply to hydrocarbons.

Figure 4 shows how to determine the normal boiling point from the vapor pressure data around an atmospheric pressure. The vapor pressure data were correlated by Antoine equation:

$$\log p[\text{kPa}] = A - \frac{B}{(T[\text{K}] + C)}$$

Then the normal boiling point at 101.325kPa of the vapor pressure was determined from Antoine equation. In order to check the reliability of the experimental apparatus and procedure, we measured the vapor pressures of pure methanol. Our measured vapor pressures agreed well with the literature values (3). The normal boiling points and Antoine constants for five fluorinated ethers and two fluorinated ketones are presented in Table 2. The vapor pressure data were fitted by Antoine equation smoothly. On the other hand, the experimental normal boiling points were compared with the Joback's estimation based on a group contribution method and the deviation was too large to use in an engineering calculation.

Conclusions

The critical properties and normal boiling points were measured using the modified static-type apparatuses, which could realize the rapid and accurate determination of these properties with a small amount of the sample. Further study on the prediction of thermodynamic properties of fluorinated compounds is important to develop new promising alternatives for CFC and HCFC.

Acknowledgment

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Literature Cited

(1) Yada, N., Kumagai, K., Tamatsu, T., Sato, H., Watanabe, K., J. Chem. Eng. Data, 36, (1991) 12

(2) Lydersen, A.L., Univ. Wisconsin Coll. Eng., Eng. Exp. Stn. Rep., (1955) 3

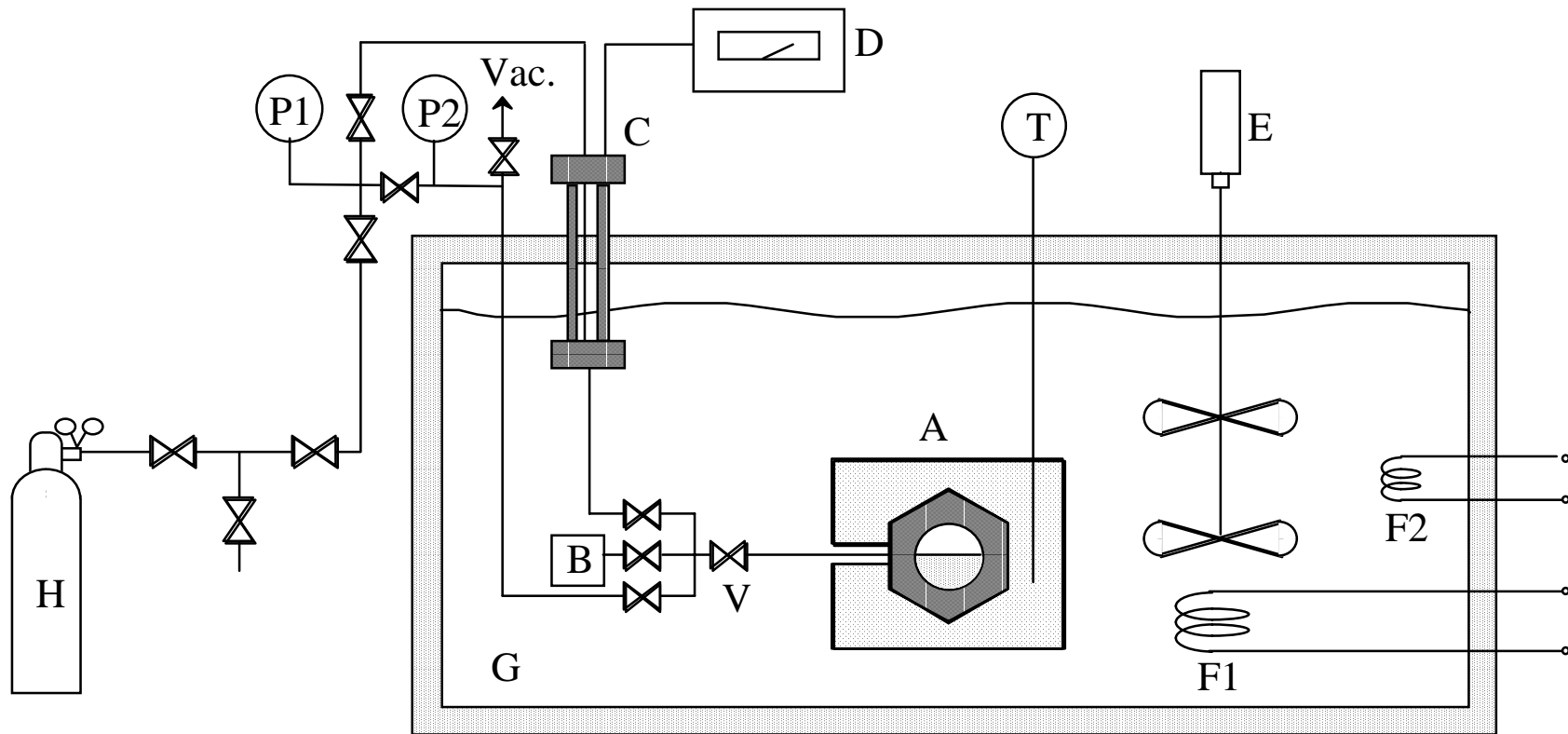
(3) Reid, R.C., Prausnitz, J.M., Poling, B.E., The properties of gases and liquids , (1987)

Table 1 Purity of samples and experimental and predicted results of critical properties

Compounds	Purity [GC%]	T _c [K]			P _c [MPa]			d _c [g/cm ³]		
		Exp.	Lydersen	Dev.	Exp.	Lydersen	Dev.	Exp.	Lydersen	Dev.
CF ₃ CF(OCF ₃)CH ₂ CF ₃	99.5	447.40	436.37	-11.03	2.140	1.998	-0.142	0.582	0.588	0.006
(CF ₃) ₃ COCH ₃	99.5	462.72	448.40	-14.32	2.366	2.415	0.049	0.558	0.554	-0.004
(CHF ₂ O) ₂ CFCF ₃	99.76	449.81	450.29	0.48	2.421	2.309	-0.112	0.571	0.581	0.010
cyc-OCHF ₂ CF ₂ OCF ₂ CF ₂ -	99.5	452.88	463.51	10.63	2.866	3.692	0.826	0.597	0.637	0.040
cyc-CF ₂ OCH(CF ₃)OCF ₂ -	99.63	435.06	466.90	31.84	2.645	3.277	0.632	0.569	0.641	0.072
CF ₃ CF ₂ C(:O)CH ₃	99.4	453.03	453.78	0.75	2.912	3.357	0.445	0.486	0.486	0.000
(CF ₃) ₂ CFC(:O)CH ₃	99.8	467.64	456.78	-10.86	2.522	2.791	0.269	0.518	0.512	-0.006
Ave.Dev.		11.42 [K]			0.354 [MPa]			0.020 [g/cm ³]		

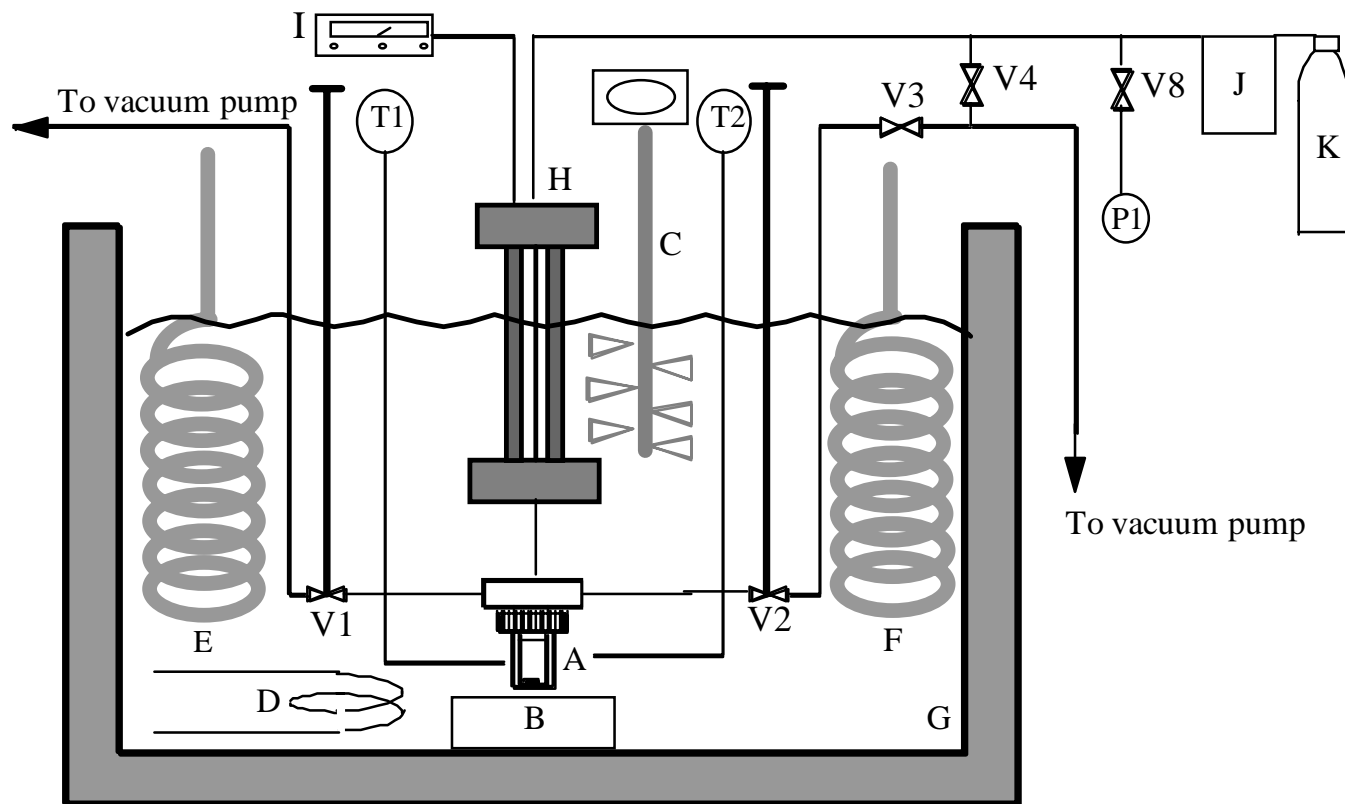
Table 2 Experimental and predicted results of normal boiling points

Compounds	Normal boiling point			Antoine constants		
	Exp.[K]	Joback [K]	Deviation [K]	A	B	C
$\text{CF}_3\text{CF}(\text{OCF}_3)\text{CH}_2\text{CF}_3$	322.72	316.0	-6.7	5.7616	934.79	-73.833
$(\text{CF}_3)_3\text{COCH}_3$	326.50	316.7	-9.8	7.4136	1942.6	32.712
$(\text{CHF}_2\text{O})_2\text{CFCH}_3$	319.95	322.6	2.6	7.7968	2192.6	58.666
cyc-OCHFCH ₂ OCF ₂ CF ₂ -	312.72	346.0	33.3	6.7157	1448.9	-5.1005
cyc-CF ₂ OCH(CF ₃)OCF ₂ -	304.98	346.0	41.0	6.0278	992.85	-58.133
$\text{CF}_3\text{CF}_2\text{C}(\text{:O})\text{CH}_3$	314.37	334.7	20.3	6.1903	1101.7	-51.093
$(\text{CF}_3)_2\text{CFC}(\text{:O})\text{CH}_3$	328.78	352.9	24.1	6.5372	1379.5	-24.354
Ave.Dev.	19.7[K]					



- | | | |
|---|--------------------------|------------------------------|
| A: View cell | F1: Main heater | P1,P2: Pressure gauges |
| B: Expansion vessel | F2: sub-heater | T: Pt resistance thermometer |
| C: Differential pressure null gauge | G: Oil bath | V: Stop valves |
| D: Differential pressure null indicator | H: Nitrogen gas cylinder | Vac.: Vacuum line |
| E: Agitator | | |

Fig. 1 Experimental apparatus for measuring critical properties



A : Equilibrium cell
 B : Magnetic stirrer
 C : Agitator
 D : Heater
 E : Cooler 1(273K)

F : Cooler 2(243K)
 G : Water bath
 H : Differential pressure cell
 I : Pressure null indicator
 J : Pressure control pack

K : Nitrogen gas cylinder
 P1 : Calibrated pressure gauge
 T1 : Calibrated thermometer
 T2 : Monitoring thermometer
 V : Valves

@Fig.2 Experimental apparatus for measuring normal boiling points

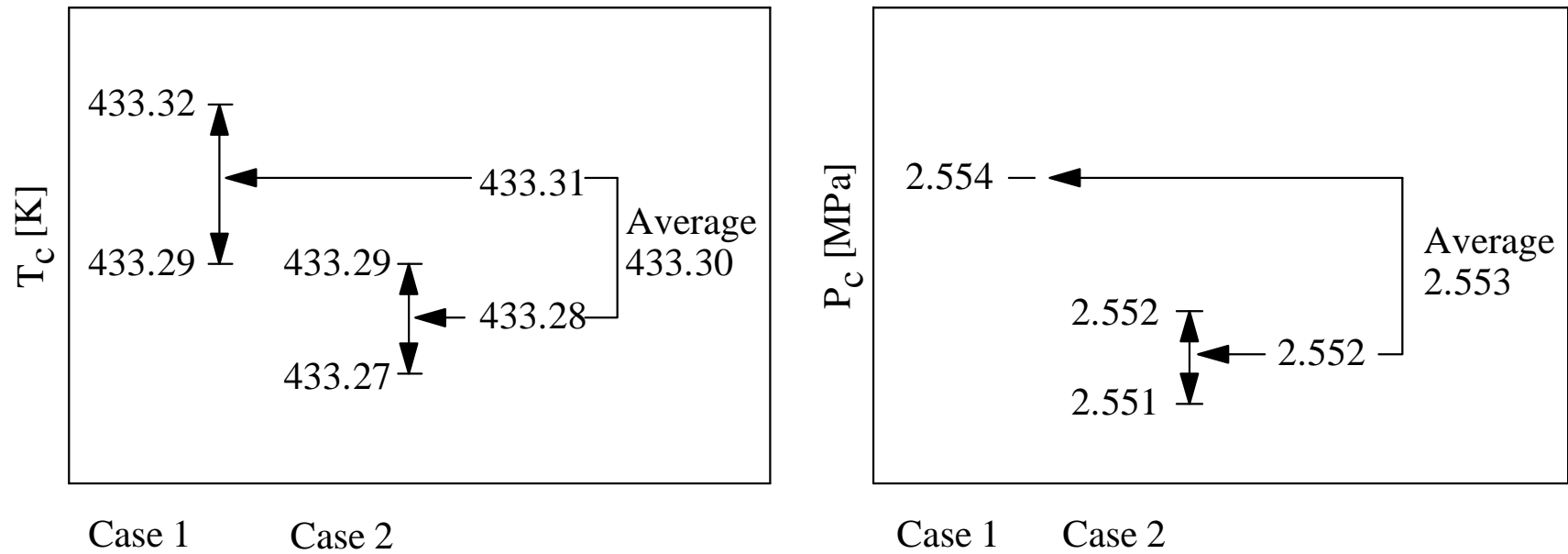


Fig.3 Uncertainty to determine critical properties of $(\text{CF}_3)_2\text{CFOCH}_3$
Case 1 : in case of increasing temperature
Case 2 : in case of decreasing temperature

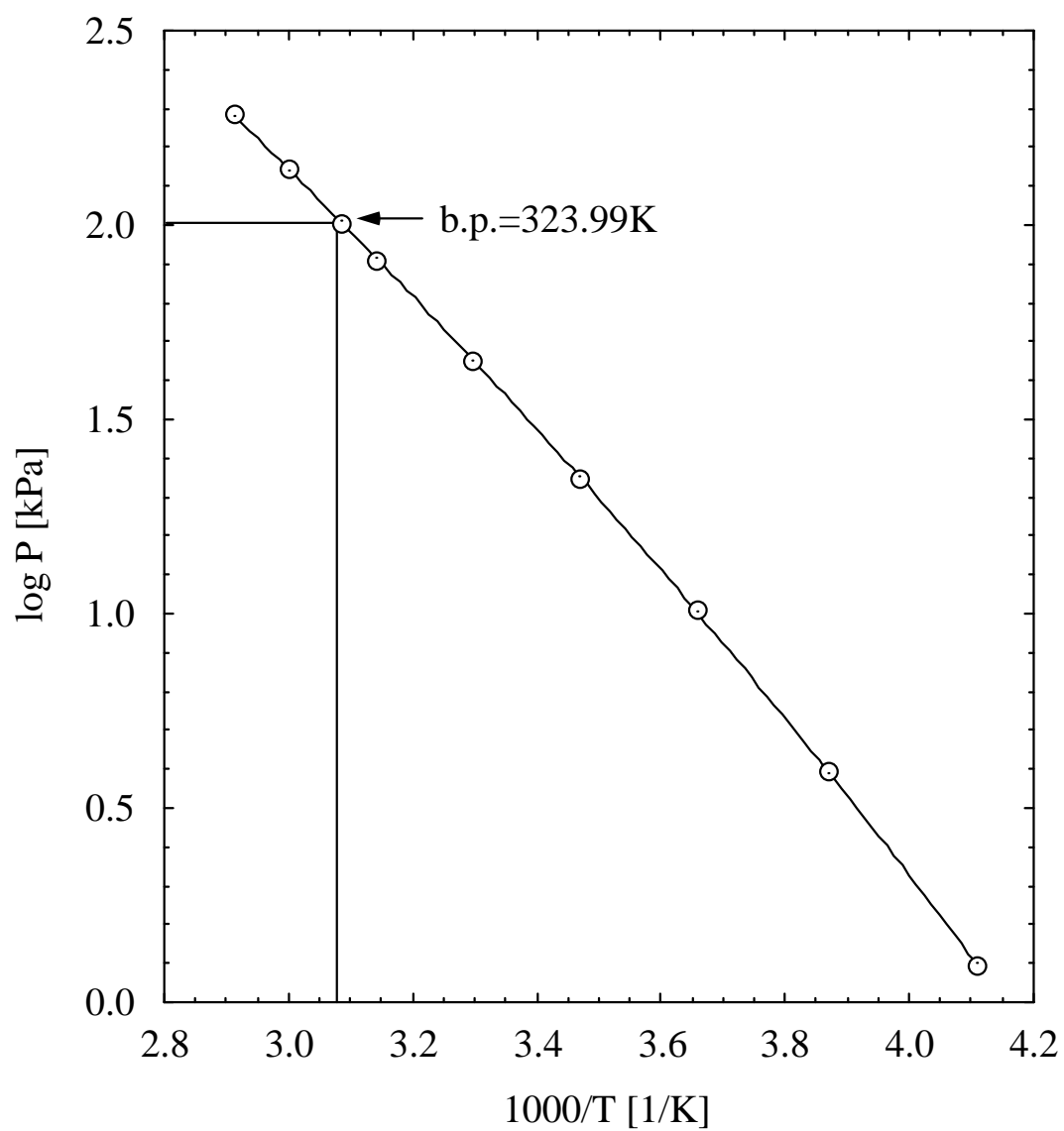


Fig.4 Vapor pressure of $(\text{CF}_3)_2\text{CHOCH}_3$